LIME-METAKAOLIN MORTARS FOR HISTORICAL BUILDINGS REPAIR: STUDY OF THE HARDENING REACTION

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ABSTRACT

Formulation of mortars with adequate durability and strength is nowadays one of the major challenges in historical buildings repair. Pozzolanic materials have been used during centuries in air lime mortars to improve their mechanic and durability characteristics.
This paper is part of an extensive work being developed in Portugal, aiming to characterize lime-metakaolin mortars to be employed for historical buildings conservation and repair.
This paper presents the results of hardening reaction study until 90 days of curing in humid conditions. The results show that in the adopted curing conditions, the hydration reaction occurs mostly for early ages of curing (28 days) while the carbonation reaction is mostly dominant for longer ages (90 days).

KEYWORDS: Metakaolin, XRD, TGA-DTA, masonry, air lime mortars, repair

1 INTRODUCTION

The importance of elaborating compatible mortars with adequate strength and durability, with the aim of improving their workability, strength and hardening, has become one of the main issues in the past few years in historic structure conservation actions.
As a matter of fact, masonry walls of historic buildings have become degraded, mainly due to poor quality of the employed building materials

(stones, bricks, mortars, etc.), specific environmental loads and improper materials used in previous restoration interventions (cement, polymeric materials, etc.).
The design and formulation of restoration materials should be approached to be compatible with the pre-existent historic materials [1]. Compatibility between the new repair mortar and the original components of masonry is desirable, being this compatibility reflected in several features: (a) chemical compatibility between the repointing mortar and the old materials (stone or brick and its bedding mortar); (b) physical compatibility, regarding processes of solubility and of water transport, (c) structural and mechanical compatibility [2, 3].
The use of aerial lime as single binder in mortars involves some well-known inconveniences, such as slow setting and carbonation times, high drying shrinkage and low mechanical strength. As a consequence restorers and scientists have worked to find alternative materials to improve the performances of aerial lime mortars, based on ancient practices. This lead to the use of pozzolans in lime based mortars, which can improve workability, mechanical strength, water permeability, salts and frost resistance in the hardened state of lime-based mortars [4, 5, 6].
This paper deals with the study of a highly reactive aluminosilicate pozzolan, metakaolin (MK), which is formed by the dehydroxilation of kaolinite at ~ 650-800ºC. Few studies regarding chemical properties of lime-metakaolin mortars have been endeavoured. In our study, lime-metakaolin mortars were prepared with different volumetric ratios and their chemical properties evaluated with the aim to formulate an adequate lime-MK-mortar composition for historical heritage purposes.

2 EXPERIMENTAL

2.1 MATERIALS AND MORTAR PREPARATION

Mortars were prepared by mixing a Portuguese commercial air lime CL (Lusical H100) and siliceous river sand as aggregate, with volumetric ratios of 1:1, 1:2 and 1:3 (binder:aggregate) and replacements of 30 and 50 wt. % of lime by commercial metakaolin (ARGICAL M1200S). Table 1 illustrates the prepared mortars identification, the binder:aggregate (B:A) ratio in volume and by weight, as well as MK in wt% of the total weight of the binder.

Table 1 Mortars identification, the binder (lime and metakaolin (MK)):aggregate ratio in volume and weigth and the percentage of MK.

Mortar identification	B:A Volume	B:A Weight	MK (wt%)
L1	1:1	1:4	0
L1MK30	1:1	1:4	30
L1MK50	1:1	1:4	50
L2	1:2	1:8	0
L2MK30	1:2	1:8	30
L2MK50	1:2	1:8	50
L3	1:3	1:12	0
L3MK30	1:3	1:12	30
L3MK50	1:3	1:12	50

The procedure regarding the mixing process was the same for all mortars: The amount of water to be added was estimated respecting the required consistency (flow values around 140 mm).
After mechanical mixing and compaction, specimens were moulded in 40mmx40mmx160mm moulds and cured at RH 90±5% and temperature of 20±3ºC. The hardening reaction was accompanied at certain ages by X-ray diffraction analysis (XRD) and simultaneous thermogravimetric and differential thermal analysis (TG-DTA).

2.1 METHODS

2.1.1 X-ray diffraction analysis

The samples were dried at 40ºC, ground in a porcelain mill and sieved at 106µm. X–ray diffractograms were obtained on a Philips PW3710 X-ray diffractometer, with 35 kV and 45 mA, using Fe-filtered CoKα radiation of wavelength λ=1.7903 Å. Diffractograms were recorded from 3-74 º2θ in 0.05 º2θ increments with 1 second per increment, in effect 0.05 º2θs^{-1}.

2.1.2 Thermogravimetric and differential thermal analysis (TG-DTA)

Simultaneous thermal analysis (STA) was conducted in a SETARAM TG-DTA analyser, under argon atmosphere, with heating rate of 10ºC/min, from room temperature to 1000ºC. Free portlandite content present in the samples was detected through mass loss in the range 380-500ºC,

corresponding to the portlandite dehydration. CO_2 content was determined in the range 500-850ºC, corresponding to the calcite decarboxylation [7,8,9,10].

3 RESULTS

3.1 X-RAY DIFFRACTION RESULTS

The XRD patterns of the formulated mortars are presented in Fig. 1, 2 and 3, respectively, showing the main hydrated phases up to 90 days of curing.
As expected, the L1 mortar (Fig.1) main hydrated phases formed are portlandite (CH) and calcite (C). The calcite presence is originated by portlandite carbonation, increasing with curing time. In Figures 2 and 3, for L2 and L3 mortars respectively, the same is verified.
As for the lime-MK mortars, the presence of hydrated phases such as calcium aluminate hydrate ($Ca_2Al(OH)_7.6.5H_2O$), monocarboaluminate ($3CaO.Al_2O_3.CaCO_3.11H_2O$) and stratlingite ($2CaO.SiO_2.Al_2O_3.8H_2O$) are found.
Sepulcre et al. [11] agree that stratlingite has beneficial properties regarding its high mechanical strength.
From the XRD results it can be seen that the MK content favours the stratlingite formation independently of the binder:aggregate mortar ratio chosen. In other words, stratlingite increases with ageing for all lime-MK blended mortar compositions, reaching its highest peak for mortar 1:1 with 50% MK content, i.e., L1MK50 and at 90 days of ageing. Regarding the monocarboaluminate and calcium aluminate hydrate (CAH) phases, it is observed that they are detected solely for mortars blended with 30% MK. disappearing with ageing.
As viewed in Figures 1 to 3, the carbonation reaction seems to be delayed at 28 days with MK introduction. However, in MK blended mortars it seems that CSH phase is overlapped with the main calcite peak, being CSH presence attributed due to a broader peak at 3.03 Å. Also, carbonation increases with ageing in all mortars.
At 90 days of curing, portlandite is not detected for 50% MK blended mortars, assuming that complete consumption may have taken place either in the hydration reaction (i.e. pozzolanic reaction) and/or in the carbonation reaction.
Nevertheless, minor phases were also observed, such as quartz, vaterite, feldspar and katoite, this last a low silica hydrogarnet, only present in 30% MK mortars at 28 days of ageing.

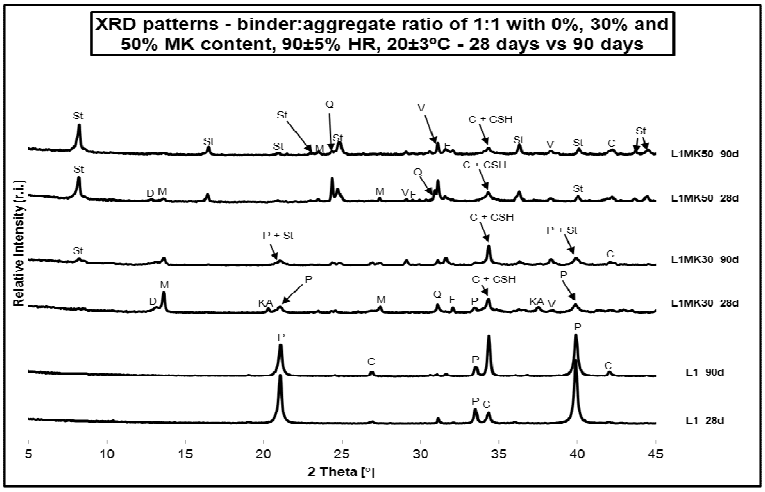

Fig. 1 – XRD patterns of mortars with a binder:aggregate 1:1 ratio and 0, 30 and 50% MK (28 days vs. 90 days of curing); St - Stratlingite ($2CaO.SiO_2.Al_2O_3.8H_2O$); M-Monocarboaluminate ($3CaO.Al_2O_3.CaCO_3.11H_2O$); D-Calcium aluminum hydrate ($Ca_2Al(OH)_7.6.5H_2O$); P-Portlandite ($Ca(OH)_2$); C – Calcite ($CaCO_3$);Q – quartz (SiO_2); F – feldspar ($KAlSi_3O_8$); V- Vaterite ($CaCO_3$).

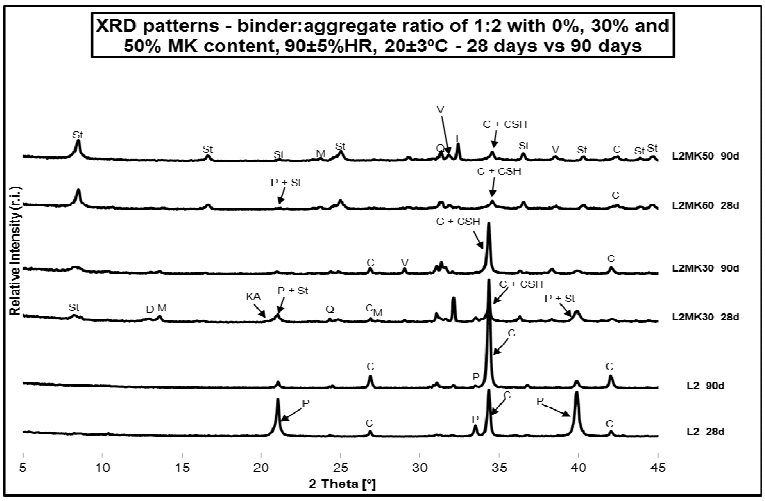

Fig. 2– XRD patterns of mortars with a binder:aggregate 1:2 ratio and 0, 30 and 50% MK (28 days vs. 90 days of curing); St - Stratlingite ($2CaO.SiO_2.Al_2O_3.8H_2O$); M-Monocarboaluminate ($3CaO.Al_2O_3.CaCO_3.11H_2O$); D-Calcium aluminum hydrate ($Ca_2Al(OH)_7.6.5H_2O$); P-Portlandite ($Ca(OH)_2$); C – Calcite ($CaCO_3$); Q – quartz (SiO_2); F – feldspar ($KAlSi_3O_8$); V- Vaterite ($CaCO_3$).

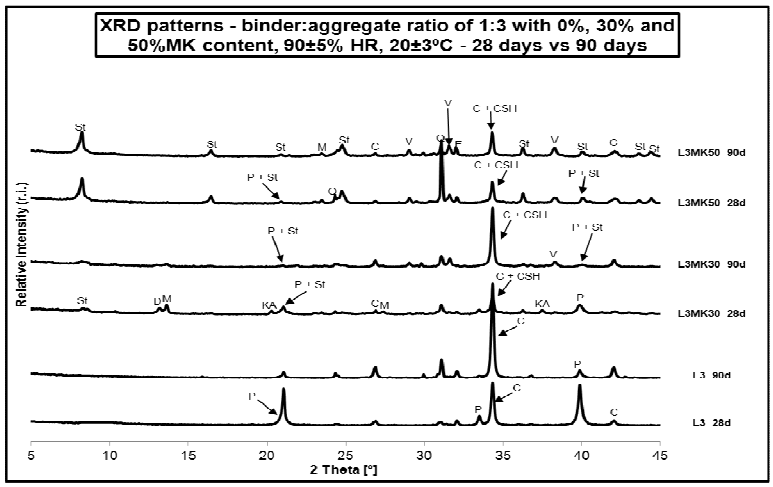

Fig. 3 – XRD patterns of mortars with a binder:aggregate 1:3 ratio and 0, 30 and 50% MK (28 days vs. 90 days of curing); St - Stratlingite ($2CaO.SiO_2.Al_2O_3.8H_2O$); M-Monocarboaluminate ($3CaO.Al_2O_3.CaCO_3.11H_2O$); D-Calcium aluminum hydrate ($Ca_2Al(OH)_7.6.5H_2O$); P-Portlandite ($Ca(OH)_2$); C – Calcite ($CaCO_3$); Q – quartz (SiO_2); F – feldspar ($KAlSi_3O_8$); V- Vaterite ($CaCO_3$).

3.2 THERMAL ANALYSIS (TG-DTA)

DTA results are shown in Figures 4, 5 and 6. The main endothermic peaks were detected at the following temperature ranges: (i) ~ 105-160ºC attributed to the dehydration peak of CSH; (ii) ~ 160-240ºC attributed to the dehydration of stratlingite, monocarboaluminate and calcium aluminium hydrate; (iii) ~ 460ºC and 750ºC attributed to portlandite and calcite decomposition, respectively [1].

From the illustrated figures, several aspects can be withdrawn. Starting with portlandite, its content is viewed to decrease with ageing and with increase of lime substitution by MK. Carbonation reaction is delayed at 28 days of curing with MK incorporation, and increases with curing time for all mortars.

As illustrated in Figures 4, 5 and 6, the corresponding endothermic pozzolanic dehydration peaks are more present for higher MK content mortars, decreasing the intensity of these peaks in the order 1:1>1:2>1:3 ratios.

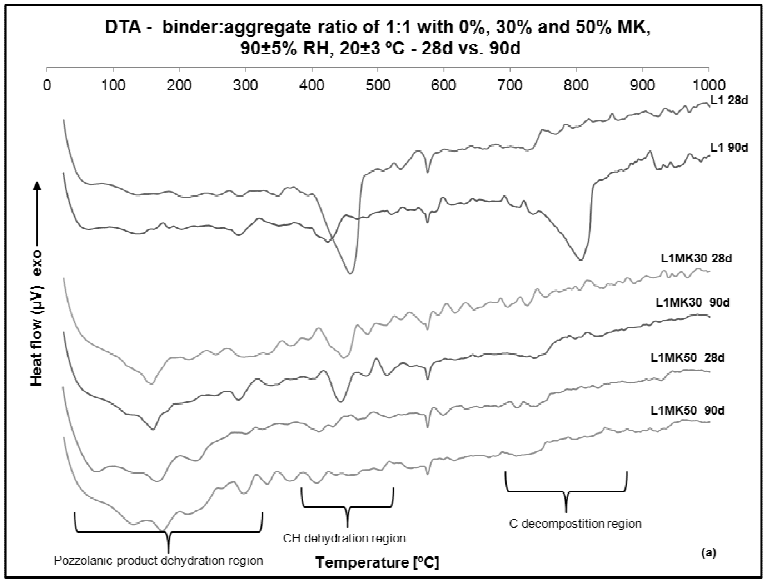

Fig.4 - DTA results of 1:1 (binder:aggregate) mortar ratio with 0, 30 and 50% MK. Pozzolanic product dehydration region (CSH, Stratlingite, Monocarboaluminate, Calcium aluminum hydrate); CH (portlandite) dehydration region; C (carbonates) decomposition region.

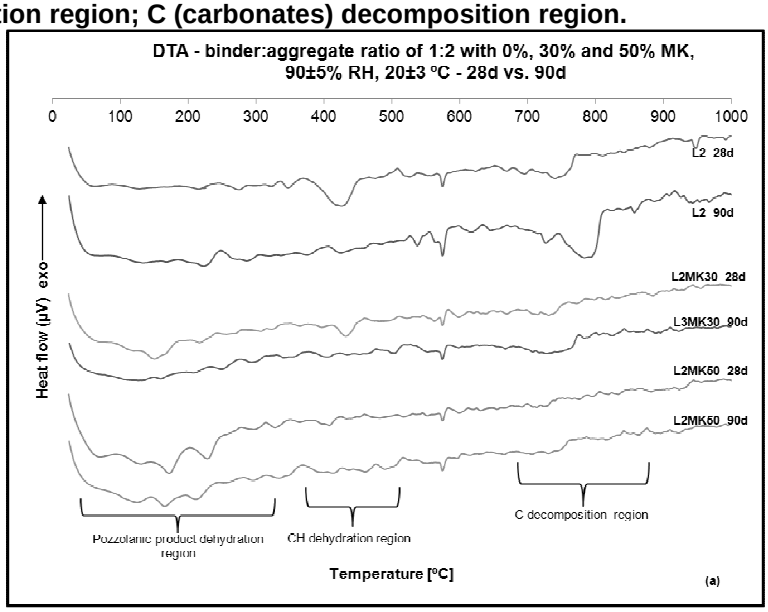

Fig.5 - DTA results of 1:2 (binder:aggregate) mortar ratio with 0, 30 and 50% MK. Pozzolanic product dehydration region (CSH, Stratlingite, Monocarboaluminate, Calcium aluminum hydrate); CH (portlandite) dehydration region; C (carbonates) decomposition region.

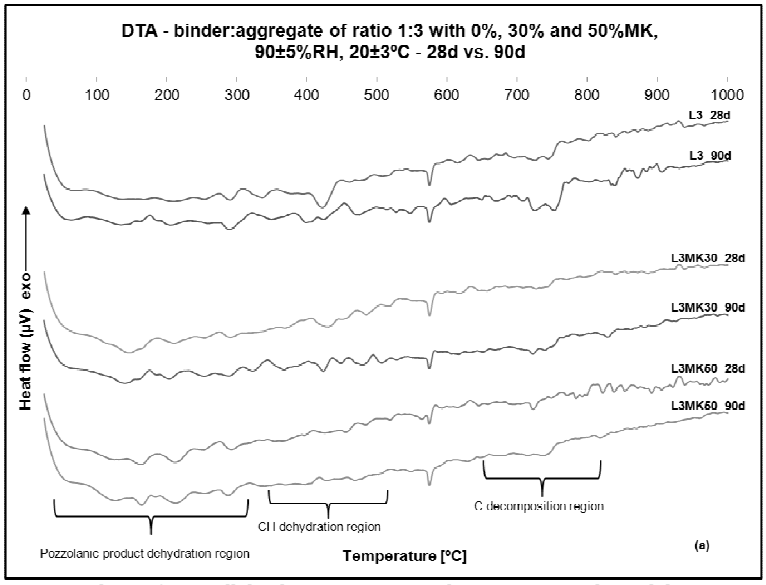

Fig.6 - DTA results of 1:3 (binder:aggregate) mortar ratio with 0, 30 and 50% MK. Pozzolanic product dehydration region (CSH, Stratlingite, Monocarboaluminate, Calcium aluminum hydrate); CH (portlandite) dehydration region; C (carbonates) decomposition region.

3.2.1 Evolution of the hardening reaction

Figures 7and 8 illustrate the evolution of the lime consumption in terms of the pozzolanic reaction versus the carbonation reaction.
From Figure 7, it can be seen that the pozzolanic reaction dominates in almost all mortars at early ages (except for the L3MK50 mortar). Mortar L1MK50 shows the highest pozzolanic reaction results.
Also, ageing promotes the increase of the carbonation reaction (Fig.8), as seen up to 90 days of curing becoming dominant at this age for practically all mortar compositions, with exception of L1MK30 and L1MK50 mortars.
Aiming to qualitatively study the evolution of the pozzolanic reaction versus the carbonation reaction, determination of consumed lime content was required according to equations 1 and 2, respectively:

(i) $CH_{poz\ (lime\ consumed\ in\ the\ pozzolanic\ reaction)} = CH_{th} - (CH_f - CH_{carb})$ [Equation 1]

- $\mathbf{CH_{th}}$ - the amount of lime used in %
- $\mathbf{CH_f}$ - free portlandite content obtained by Equation 1.1

ii) $CH_{f\ (free\ portlandite\ content)} = ML_{(400\text{-}500ºC)} \times MM_{(CH)}/MM_{(H2O)}$ [Equation 1.1.]

- **$ML_{(400\text{-}500ºC)}$** - mass loss attributed to portlandite dehydration in the temperature range 400-500ºC
- **$MM_{(CH)}$** - molar mass of portlandite and
- **$MM_{(H2O)}$** - the molar mass of water

(iii) $CH_{carb\ (carbonated\ portlandite\ content)} = ML_{(500\text{-}850ºC)} \times MM_{(CaCO3)}/MM_{(CO2)}$
[Equation 1.2]

- **$ML_{(500\text{-}850ºC)}$** - CO_2 mass loss in the temperature range 500-850ºC, corresponding to calcite decarboxylation.
- **$MM_{(CaCO3)}$** - the molar mass of calcite,
- **$MM_{(CO2)}$** - the molar mass of carbon dioxide.

(iv) $CH_{c\ (lime\ consumed\ in\ the\ carbonation\ reaction)} = ML_{(500\text{-}850ºC)} \times MM_{CH} / MM_{(CaCO3)}$
[Equation 2]

- **$ML_{(500\text{-}850ºC)}$** - the mass loss attributed to calcite decarboxylation in the temperature range 500-850ºC.
- **$MM_{(CH)}$** - molar mass of portlandite,
- **$MM_{(CaCO3)}$** - the molar mass of calcite.

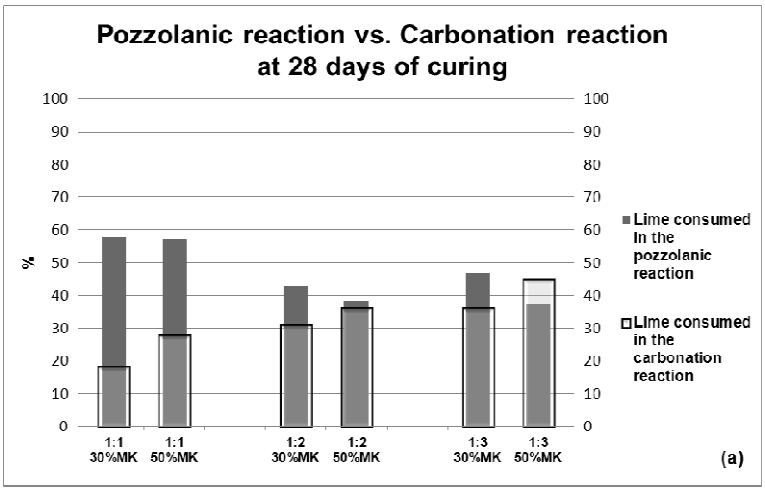

Fig 7 –Pozzolanic reaction versus carbonation reaction at 28 days of curing.

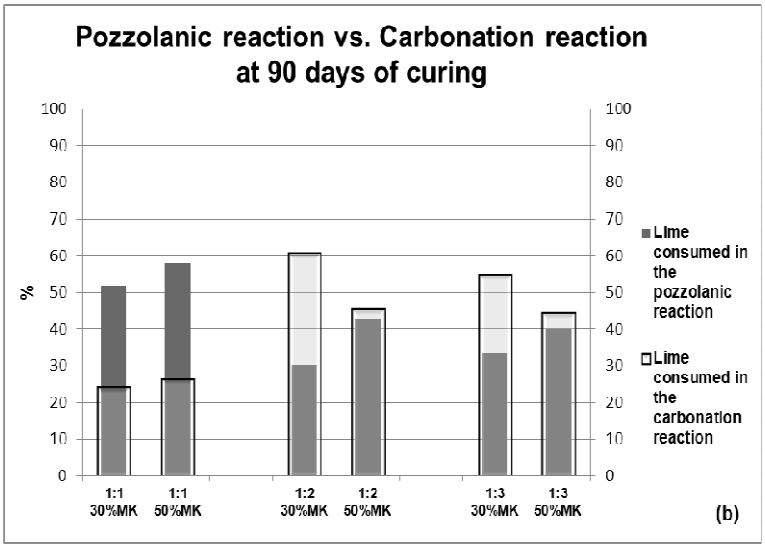

Fig 8 - Pozzolanic reaction versus carbonation reaction at 90 days of curing.

4. CONCLUSIONS

According to the XRD results the main hydrated phases formed in lime-MK blended mortars are stratlingite, calcium aluminate hydrate, monocarboaluminate and portlandite. These phases are chemically compatible with old renders and masonries. Stratlingite, a hydrated compound responsible for the high mechanical resistance in the lime-MK mortars, was favoured by mortars possessing high MK content and with increasing ageing, independently of the chosen binder:aggregate mortar ratio. This hydrated phases was found to be more abundant with the 1:1 binder:aggregate mortar ratio.

The TG-DTA results showed that, with the humid curing conditions used, the pozzolanic reaction is favoured in relation to the carbonation reaction at early ages of curing (28 days), reverting its dominance to the carbonation reaction at longer curing times (90 days) for almost all mortar compositions, except L1MK30 and L1MK50. Also, according to the results obtained, the mortar with 1:1 binder:aggregate ratio and 50 MK wt. % appears to be the mortar composition showing the highest pozzolanic reaction.

Physical and mechanical characterization is being developed, which should be evaluated and taken into account before any recommendation for application in the work site.

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